

## Accomplishments in Support of NASA ACMAP under NRA-97-MTPE-07

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Over the past three years, the primary foci of our research have been on studies of stratospheric processes and the potential effects of natural perturbations and human related activities on global stratospheric ozone, on interactions between atmospheric chemistry, atmospheric composition and concerns about climate change, and, to a lesser degree, on studies of tropospheric processes. Published research articles are listed.

### ***Research Studies and Journal Articles***

#### **Changes in Stratospheric Chemistry**

##### *Analyses of changes in bromine chemistry*

Patten, K.O., D.J. Wuebbles, Z. Li, and S.P. Sander, Effects of recent bromine chemistry experiments on modeled stratospheric ozone. To appear in book resulting from the Proceedings of the Quadrennial Ozone Symposium, L'Aquila, Italy, September 12-21, 1996, in press, 1997.

Patten, K. O., Z. Li, D. J. Wuebbles, and S. P. Sander, Effects of Some Recent Chemistry Developments on Methyl Bromide Ozone Depletion Potential, 1997 Methyl Bromide State of the Science Workshop, Monterey, CA, June 10-12, 1997; journal paper in progress

Given the potential importance of chemical processes involving bromine on stratospheric ozone in the lower stratosphere, it is important to consider how changes in our understanding of bromine reactions may affect ozone and the effects of human related emissions on ozone (from  $\text{CH}_3\text{Br}$  and other chemicals). Two studies using the two-dimensional model have addressed the effects of a series of new laboratory measurements involving brominated species on lower stratospheric chemistry.

##### *Ozone photolysis*

Recent experimental data have suggested that a change in the modeled treatment of the photolysis quantum yield of singlet oxygen atom ( $\text{O}^1\text{D}$ ) from ozone ( $\text{O}_3$ ) is necessary. Previous recommended photochemistry (DeMore et al., 1994) stated that this quantum yield decreased steeply for wavelengths beyond 300 nm and became zero at 305 nm. However, Michelsen et al. (1994) found a temperature-dependent quantum yield from 300 to 320 nm, consistent with a contribution from "hot-band" absorption by  $\text{O}_3$  possessing at least one quantum of vibrational excitation. The increase in the  $\text{O}^1\text{D}$  yield thus should cause significant modifications in the trace gas distributions derived in atmospheric chemical-transport models, as confirmed in preliminary calculations with our two-dimensional model. A journal article is to be submitted within coming months.

#### **Evaluation of CFC and Halon Replacements**

Wuebbles, D.J., P.S. Connell, and K.O. Patten, Evaluating the potential effects of halon replacements on the global environment. In *Halon Replacements: Technology and Science*, A.W. Miziolek and W. Tsang, eds., American Chemical Society, 1995.

Connell, P.S., D.E. Kinnison, D.J. Bergmann, K.O. Patten, D.J. Wuebbles, R.G. Daniel, C.K. Williamson, A.W. Miziolek, and R.E. Huie, Environmental effects of halon replacements: considerations for advanced agents and the Ozone Depletion Potential of  $\text{CF}_3\text{I}$ , Proceedings of the Halon Options Technical Working Conference, Albuquerque, N.M., May 7-9, 1996.

Connell, P. S., D. E. Kinnison, D. J. Bergmann, K. O. Patten, D. J. Wuebbles, The response of stratospheric ozone to surface emissions of  $\text{CH}_3\text{I}$  and  $\text{CF}_3\text{I}$  in the LLNL 2-d chemistry/transport model, to appear in book resulting from the Proceedings of the Quadrennial Ozone Symposium, L'Aquila, Italy, September 12-21, 1996, in press, 1997. Journal article in progress.

Wuebbles, D.J., A.K. Jain, K.O. Patten, and P.S. Connell, Evaluation of Ozone Depletion Potentials for Chlorobromomethane ( $\text{CH}_2\text{ClBr}$ ) and 1-Bromo-Propane ( $\text{CH}_2\text{BrCH}_2\text{CH}_3$ ). *Atmos. Environ.*, in press, 1997.

A series of studies have evaluated the potential effects of CFC and Halon replacements on the global environment. Ozone Depletion Potentials were evaluated for many compounds (e.g., for WMO, 1995).

Calm, J.M., D.J. Wuebbles, and A.K. Jain, Impacts on global ozone and climate from use and emission of 2,2-dichloro-1,1,1-trifluoroethane (HCFC-123) emissions. *Climatic Change*, submitted, 1997.

Wuebbles, D.J., and J.M. Calm, An environmental rationale for retention of endangered chemical species. *Science*, submitted, 1997.

These two papers, currently under review, challenge the current approach of the Montreal Protocol in its consideration of replacement compounds, suggesting that some of the HCFCs may provide important societal gains while having insignificant effects on ozone and climate. These papers, through examples, also suggest that ozone and climate effects of a chemical should both be considered in evaluating policy.

#### The Maunder Minimum (and evaluations of solar flux changes)

Wuebbles, D.J., C.-F. Wei, and K.O. Patten, The distribution of stratospheric ozone during the Maunder Minimum. To appear in book resulting from the Proceedings of the Quadrennial Ozone Symposium, L'Aquila, Italy, September 12-21, 1996, in press, 1997. Journal article in progress.

This study is the first evaluation of the impact of reduced solar radiation on ozone during the Maunder Minimum (about 1645-1715). This study suggests there was a 3 % decrease in total ozone during this period. Such solar events are likely to happen again. A new analysis of the 27-day and 11-year solar cycles is also underway.

#### Stratospheric Chemical Interactions

Wuebbles, D.J., and D.E. Kinnison, Predictions of future ozone changes. *Int. J. Environ. Studies*, 51, 269-283, 1996.

Considine, D.B., P.S. Connell, C.H. Jackman, D.E. Kinnison, G. Pitari, L. Ricciardulli, X.X. Tie, G. Visconti, and D.J. Wuebbles, An intercomparison of the effects of polar stratospheric cloud parameterizations on model predictions of High Speed Civil Transport impacts. *J. Geophys. Res.*, in revision, 1997.

The Wuebbles and Kinnison study uses the two-dimensional model and the chlorine-bromine loading concept to examine future projections of ozone. The Considine et al. study compares the representation of PSCs in several stratospheric chemical-transport models. It includes the climatological treatment of PSC processes originally developed at LLNL.

#### Trends in Ozone and Temperature

Miller, A.J., G.C. Tiao, G.C. Reinsel, D. Wuebbles, L. Bishop, J. Kerr, R.M. Nagatani, J.J. and C.L. Mateer, Comparisons of observed ozone trends in the stratosphere through examination of Umkehr and balloon ozonesonde data. *J. Geophys. Res.*, 100, 11,209-11,217, 1995.

Miller, A.J., R.M. Nagatani, G.C. Tiao, X.F. Niu, G.C. Reinsel, D. Wuebbles, K. Grant, L. Bishop, J. Kerr, W. Planet and R. McPeters, Trends of stratospheric ozone and temperature. In *Diagnostic Tools in Atmospheric Physics*, edited by G. Fiocco and G. Visconti. IOS Press, Amsterdam, 1995.

Miller, A.J., S.M. Hollandsworth, L.E. Flynn, G.C. Tiao, G.C. Reinsel, L. Bishop, R.D. McPeters, W.G. Planet, J.J. DeLuisi, C.L. Mateer, D. Wuebbles, J. Kerr, and R.M. Nagatani, Comparisons of observed ozone trends and solar effects in the stratosphere through examination of ground-based Umkehr and combined SBUV, SBUV/2 satellite data. *J. Geophys. Res.*, 101, 9017-9021, 1996.

Miller, A.J., L.E. Flynn, S.M. Hollandsworth, J.J. DeLuisi, I.V. Petropavlovskikh, G.C. Tiao, G.C. Reinsel, D.J. Wuebbles, J. Kerr, R.M. Nagatani, L. Bishop, and C.H. Jackman, Information content of Umkehr and SBUV(2) satellite data for ozone trends and solar responses in the stratosphere. *J. Geophys. Res.*, in press, 1997.

These studies are part of our continuing coordination in using statistical techniques on satellite, ground-based, and balloon datasets to examine trends in total ozone, in the distribution of ozone, and in temperature. Recent studies indicate an overall better picture of the trends in ozone over the last two decades. A study in progress is using results from our two-dimensional model study of the effects on ozone resulting from the Mt. Pinatubo eruption (Kinnison et al., 1994) to examine how representing these effects can reduce uncertainties in determining the ozone trends due to human activities during the 1990s.

### Chemistry-Climate Interactions

- Wuebbles, D.J., Air pollution and climate change. Chapter 14 in *Composition, Chemistry, and Climate of the Atmosphere Air Pollution, Air Chemistry, and Global Change*, H.B. Singh, editor, Von Nostrand Reinhold Publishers, 1995.
- Wuebbles, D.J., A.K. Jain, K.E. Grant, K.O. Patten, Sensitivity of direct global warming potentials to key uncertainties. *Climate Change*, 29, 265-297, 1995.
- Wuebbles, D.J., Weighing functions for ozone depletion and greenhouse gas effects on climate. *Annual Reviews of Energy and the Environment*, 20, 45-70, 1995.
- Wuebbles, D.J., and A.K. Jain, Concerns about climate change and SF<sub>6</sub>. Proceedings of the Conference on SF<sub>6</sub> Use in Electrical Transmission and Distribution Systems. Washington, D.C., August 9-10, 1995.
- Song, N., D. O'C. Starr, D. Wuebbles, A. Williams, and S. Larson, Volcanic aerosols and interannual variation of high clouds. *Geophys. Res. Lett.*, 23, 2657-2660, 1996.
- Wuebbles, D.J., Three-dimensional chemistry in the greenhouse. *Climatic Change*, 34, 397-404, 1996.
- Wuebbles, D.J., and N. Rosenberg, The natural science of climate change. In *Human Choice and Climate Change: An International Assessment*, in press, 1997.
- Wuebbles, D.J., B.J.Y. Wuebbles, and N. Rosenberg, Global climate change and the world food supply, prepared for publication in special book on Agriculture and World Food Supply, 1997.
- Grossman, A., K.E. Grant, and D.J. Wuebbles, Radiative forcing calculations for CH<sub>3</sub>Cl and CH<sub>3</sub>Br. *J. Geophys. Res.*, 102, 13651-13656, 1997.

These chemistry-climate interaction studies are primarily aimed at examining the relationship between atmospheric composition, atmospheric chemistry and radiative forcing on climate. The Wuebbles (1995), Wuebbles and Rosenberg (1997) and Wuebbles et al. (1997) papers are overviews of the concerns about climate change including discussion of current knowledge on the effects of chemistry-climate interactions. Song et al. (1996) uses SAGE II and other data to examine the effects of volcanic aerosols in affecting the extent of cirrus clouds. Wuebbles (1996) discusses the necessity of three-dimensional models in representing the interactions between tropospheric chemistry and climate change. Wuebbles et al. (1995), Wuebbles (1995), Wuebbles and Jain (1995), and Grossman et al. (1997) discuss and evaluate Global Warming Potentials associated with various compounds of interest.

### **National and International Assessments**

- World Meteorological Organization (lead author one chapter and contributing authors on several), *Scientific Assessment of Ozone Depletion: 1994*. World Meteorological Organization report, Global Ozone Research and Monitoring Project-Report No. 37, 1995.
- Intergovernmental Panel on Climate Change (IPCC, lead author one chapter and contributing author on another), *Climate Change 1994: Radiative Forcing of Climate Change*, Cambridge University Press, 1995.
- Stolarski, R., editor (contributing author), 1995 *Scientific Assessment of the Atmospheric Effects of Stratospheric Aircraft*. NASA Reference Publication 1381, Washington, D.C., 1995.
- Intergovernmental Panel on Climate Change (IPCC, lead author of one chapter), *Climate Change 1995: The Science of Climate Change*. J.T. Houghton, L.G. Meira Filho, B.A. Callander, N. Harris, A. Kattenberg, and K. Maskell, editors, Cambridge University Press, Cambridge, U.K., 1996.

Friedl, R.R., editor (lead author), *1996 Interim Assessment of the Atmospheric Effects of Subsonic Aircraft*. NASA Reference Publication 1400, 1997.

National Academy of Sciences (lead author), *Fire Suppression Substitutes and Alternatives to Halon for U.S. Navy Applications*. National Academy Press, Washington, D.C., 1997.

NASA ACMAP support has been instrumental in our active participation in national and international assessment related to concerns about ozone and climate change. Along with being a lead author on most of the assessments referenced above, we also provided modeling analyses of effects on ozone for various scenarios, evaluations of Ozone Depletion Potentials, evaluations of Global Warming Potentials, and analyses of chlorine-bromine loading. Primary support for the aircraft assessments came from the AEAP Program but this was leveraged by our support from NASA ACMAP.

### ***Model Development***

In the past three years, several major changes to the two-dimensional model have occurred and several additional improvements are currently in progress. Included below are references to papers describing the redesign of the dynamical treatment in the model. These include a representation of  $K_{yy}$  now included in the model based on representation of planetary wavenumbers 1 and 2 (Li et al., 1995). A follow-up paper is currently in progress further describing the effects of the treatment of multiple planetary waves on stratospheric transport and the distributions of stratospheric constituents. The results of these studies were included in a major rewrite of the two-dimensional model over the last few years. Temperature feedback processes were recently reincorporated into the model by one of our University of Illinois graduate students.

Li, L., T.R. Nathan, and D.J. Wuebbles, Topographically forced planetary wave breaking in the stratosphere. *Geophys. Res. Lett.*, 22, 2953-2956, 1995.

Choi, W-K, D.A. Rotman, and D.J. Wuebbles, Eddy heat flux convergence in the troposphere and its effect on the meridional circulation and ozone distribution. *J. Atmos. Sci.*, 52, 4472-4481, 1995.

Choi, W-K, D.A. Rotman, and D.J. Wuebbles, Calculation of a residual mean circulation for a zonal-mean tracer transport model. Lawrence Livermore National Laboratory Report UCRL-ID-119565, 1995.

Several improvements to the 2-D model are currently in progress in addition to initial studies for development of the PSC and oxygen photolysis treatments described later. We are reevaluating the parameterization for latent heat effects on the derived circulation; derivations of latent heating from the NASA Goddard Data Assimilation Organization (DAO) is being tested in the new parameterization. We are adding a parameterization of convective processes to the model and a representation of hydrocarbon and other relevant tropospheric chemistry. We are also currently involved in the NASA ACMAP sponsored Modeling and Measurements II Workshop comparison of models and atmospheric data.